

**PROCESS FOR THE PURIFICATION OF A CRUDE CARBOXYLIC ACID
SLURRY**

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FIELD OF INVENTION

The present invention relates to a process for the purification of a
10 crude carboxylic acid slurry. More specifically, the present invention relates
to a process for the purification of a crude carboxylic acid slurry by utilizing
a solid-liquid displacement zone between a primary oxidation zone and a
staged oxidation zone.

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BACKGROUND OF THE INVENTION:

Terephthalic acid is commercially produced by oxidation of
paraxylene in the presence of a catalyst, such as, for example, Co, Mn, Br
and a solvent. Terephthalic acid used in the production of polyester fibers,
20 films, and resins must be further treated to remove impurities present due to
the oxidation of para-xylene. Typical commercial process produce a crude
terephthalic acid then dissolve the solid crude terephthalic acid in water at
high temperatures and pressures, hydrogenate the resultant solution, cool
and crystallize the terephthalic acid product out of solution, and separate

the solid terephthalic product from the liquid as discussed in U.S. Patent No. 3,584,039 herein incorporated by reference.

A number of processes for producing the purified terephthalic acid solid have been developed and are commercially available. Usually, the purified terephthalic acid solid is produced in a multi-step process wherein a crude terephthalic acid is produced. The crude terephthalic acid does not have sufficient quality for direct use as starting material in commercial polyethylene terephthalate(PET). Instead, the crude terephthalic acid is usually refined to purified terephthalic acid solid.

Liquid phase oxidation of p-xylene produces crude terephthalic acid. The crude terephthalic acid is dissolved in water and hydrogenated for the purpose of converting 4-carboxybenzaldehyde to p-toluic acid, which is a more water-soluble derivative, and for the purpose of converting characteristically yellow compounds to colorless derivatives. Significant 4-carboxybenzaldehyde and p-toluic acid in the final purified terephthalic acid product is particularly detrimental to polymerization processes as they may act as chain terminators during the condensation reaction between terephthalic acid and ethylene glycol in the production of PET. Typical purified terephthalic acid contains on a weight basis less than 250 parts per million (ppm) 4-carboxybenzaldehyde and less than 150 ppm p-toluic acid.

The crude terephthalic acid typically contains on a weight basis from about 800 to 7,000 parts per million (ppm) 4-carboxybenzaldehyde and about 200 to 1,500 ppm p-toluic acid as the main impurities. The crude

terephthalic acid also contains lesser amounts, about 20-200 ppm range, of aromatic compounds having the structures derived from benzil, fluorenone, and/or anthraquinone, which are characteristically yellow compounds as impurities resulting from coupling side reactions occurring during oxidation of p-xylene

Such a purification process typically comprises adding water to the crude terephthalic acid to form a crude terephthalic acid slurry, which is heated to dissolve the crude terephthalic acid. The crude terephthalic acid solution is then passed to a reactor zone in which the solution is contacted with hydrogen in the presence of a heterogeneous catalyst at temperatures of about 200° to about 375° C. This reduction step converts the various color causing compounds present in the crude terephthalic acid to colorless derivatives. The principal impurity, 4-carboxybenzaldehyde, is converted to p-toluic acid.

Typical crude terephthalic acid contains excessive amounts of both 4-carboxybenzaldehyde and p-toluic acid on a weight basis. Therefore, to achieve less than 250 ppmw 4-carboxybenzaldehyde and less than 150 ppmw p-toluic acid in the purified terephthalic acid requires mechanisms for purifying the crude terephthalic acid and removing the contaminants.

In many processes, colored impurities are hydrogenated to colorless derivatives and leave the process with the terephthalic acid solid product and waste water streams. However, one embodiment of this invention provides an attractive process to produce a purified carboxylic acid slurry by

utilizing a solid-liquid displacement zone comprising a solid-liquid separator after oxidation of a crude carboxylic acid slurry product and prior to final filtration and drying without the use of an hydrogenation step.

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SUMMARY OF THE INVENTION

In one embodiment of the invention, a process to produce the purified carboxylic acid product is provided without the use of hydrogenation of the terephthalic acid or a process separating impurities from oxidation solvent as disclosed in U.S. patent #3,584,039.

In another embodiment of this invention, a process to produce a slurry product is provided. The process comprises removing impurities from a crude carboxylic acid slurry in a solid-liquid displacement zone to form a slurry product; wherein there is a substantial absence of terephthalic acid and isophthalic acid in the crude carboxylic acid slurry.

In another embodiment of this invention, a process to produce a purified carboxylic acid product is provided. The process comprises:

(a) removing impurities from a crude carboxylic acid slurry in a solid-liquid displacement zone to form a slurry product; wherein there is a substantial absence of terephthalic acid and isophthalic acid in the crude carboxylic acid slurry;

(b) oxidizing the slurry product in a staged oxidation zone to form a staged oxidation product;

(c) crystallizing the staged oxidation product in a crystallization zone to form a crystallized product.

5 In another embodiment of this invention, a process to produce a purified carboxylic acid slurry is provided. The process comprises:

(a) removing in a solid-liquid displacement zone impurities from a crude carboxylic acid slurry to form a slurry product; wherein the crude carboxylic acid slurry comprises terephthalic acid, catalyst, acetic acid, and
10 impurities that is withdrawn at a temperature between about 140°C and about 170°C from the oxidation of paraxylene in a primary oxidation zone; wherein there is a substantial absence of terephthalic acid and isophthalic acid in the crude carboxylic acid slurry;

(b) oxidizing the slurry product in a staged oxidation zone to form
15 a staged oxidation product; wherein the oxidizing is conducted at a temperature between about 190°C to about 280 °C; and wherein the oxidizing is at a higher temperature in the staged oxidation zone than in the primary oxidation zone;

(c) crystallizing the staged oxidation product in a crystallization
20 zone to form a crystallized product;

(d) cooling the crystallized product in a cooling zone to form a cooled purified carboxylic acid slurry; and

(e) filtering and optionally drying the cooled purified carboxylic slurry in a filtration and drying zone to remove a portion of the solvent from the cooled carboxylic acid slurry to produce the purified carboxylic acid product.

5 In yet another embodiment of this invention, a process to produce a purified carboxylic acid product is provided. The process comprises:

(a) oxidizing an aromatic feed stock in a primary oxidation zone to form a crude carboxylic acid slurry; wherein the crude carboxylic acid slurry comprises terephthalic acid; wherein the oxidizing is conducted at a
10 temperature between about 120°C to about 190 °C; wherein there is a substantial absence of terephthalic acid and isophthalic acid in the crude carboxylic acid slurry;

(b) removing in a solid-liquid displacement zone impurities from a crude carboxylic acid slurry to form a slurry product; wherein the crude
15 carboxylic acid slurry comprises terephthalic acid, catalyst, acetic acid, and impurities that is withdrawn at a temperature between about 140°C and about 170°C from the oxidation of paraxylene in a primary oxidation zone;

(c) oxidizing the slurry product in a staged oxidation zone to form a staged oxidation product; wherein the oxidizing is conducted at a
20 temperature between about 190°C to about 280 °C; and wherein the oxidizing is at a higher temperature in the staged oxidation zone than in the primary oxidation zone

(d) crystallizing the staged oxidation product in a crystallization zone to form a crystallized product;

(e) cooling the crystallized product in a cooling zone to form a cooled purified carboxylic acid slurry; and

5 (f) filtering and optionally drying the cooled purified carboxylic slurry in a filtration and drying zone to remove a portion of the solvent from the cooled carboxylic acid slurry to produce the purified carboxylic acid product.

10 These objects, and other objects, will become more apparent to others with ordinary skill in the art after reading this disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

15 Figure 1 is a schematic of the inventive process for the oxidative purification of carboxylic acid wherein a solid-liquid displacement zone **40** is utilized between the primary oxidation zone **20** and the staged oxidation zone **80**.

20 DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a process for the purification of a crude carboxylic acid slurry **30**. The process comprises displacing a mother

liquor from the crude carboxylic acid slurry in a solid-liquid displacement zone **40** to form a slurry product **70**.

Crude terephthalic acid is conventionally made via the liquid phase air oxidation of paraxylene in the presence of a suitable oxidation catalyst.

5 Suitable catalysts comprises at least one selected from, but are not limited to, cobalt, bromine and manganese compounds, which are soluble in the selected solvent. Suitable solvents include, but are not limited to, aliphatic mono-carboxylic acids, preferably containing 2 to 6 carbon atoms, or benzoic acid and mixtures thereof and mixtures of these compounds with
10 water. Preferably the solvent is acetic acid mixed with water, in a ratio of about 5:1 to about 25:1, preferably between about 8:1 and about 20:1. Throughout the specification acetic acid will be referred to as the solvent. However, it should be appreciated that other suitable solvents, such as those disclosed previously, may also be utilized. Patents disclosing the
15 production of terephthalic acid such as U.S patent #4,158,738 and #3,996,271 are hereby incorporated by reference.

In an embodiment of this invention, a process to produce slurry product **70** is provided in Figure 1. The process comprises removing impurities from a crude carboxylic acid slurry **30** in a solid-liquid
20 displacement zone **40** to form a slurry product **70**; wherein the slurry product **70** is formed without a hydrogenation step.

The solid-liquid displacement zone **40**, impurities, crude carboxylic acid slurry **30**, and slurry product **70** are all described subsequently in this disclosure.

In another embodiment of this invention a process to produce a
5 purified carboxylic acid product **230** is provided in Figure 1. The process comprises:

Step (a) comprises removing impurities from a crude carboxylic acid slurry **30** in an solid-liquid displacement zone **40** to form a slurry product **70**;

A crude carboxylic acid slurry **30** comprises at least one carboxylic
10 acid, catalyst, at least one solvent, and impurities is withdrawn via line **30**.
The impurities typically comprise at least one or more of the following compounds: 4-carboxybenzaldehyde(4-CBA), trimellitic acid(TMA), and 2,6-dicarboxyfluorenone(2,6-DCF). The solvent typically comprises acetic acid, but can be any solvent that has been previously mentioned.

15 The crude carboxylic acid slurry **30** is produced by oxidizing in a primary oxidation zone **20** an aromatic feed stock **10**. In one embodiment, the aromatic feedstock comprises paraxylene. The primary oxidation zone **20** comprises at least one oxidation reactor, and the crude carboxylic acid slurry **30** comprises at least one carboxylic acid. The oxidation reactor can
20 be operated at temperatures between about 120°C to about 200°C, preferably about 140°C to about 170°C. Typically the aromatic feed stock **10** is paraxylene and the carboxylic acid is terephthalic acid. In one

embodiment of the invention the primary oxidation zone comprises a bubble column.

Therefore, when terephthalic acid is utilized, the crude carboxylic acid slurry **30** would be referred to as crude terephthalic acid slurry and the
5 purified carboxylic acid product **230** would be referred to as a purified terephthalic acid product.

Carboxylic acids include aromatic carboxylic acids produced via controlled oxidation of an organic substrate. Such aromatic carboxylic acids include compounds with at least one carboxylic acid group attached to a
10 carbon atom that is part of an aromatic ring, preferably having at least 6 carbon atoms, even more preferably having only carbon atoms. Suitable examples of such aromatic rings include, but are not limited to, benzene; biphenyl, terphenyl, naphthalene, and other carbon-based fused aromatic rings. Examples of suitable carboxylic acids include, but are not limited to,
15 terephthalic acid, benzoic acid, p-toluic, isophthalic acid, trimellitic acid, naphthalene dicarboxylic acid, and 2,5-diphenyl-terephthalic acid. Each of the embodiments of this invention can be practiced wherein there is a substantial absence of terephthalic acid and isophthalic acid in the crude carboxylic acid slurry. When the term substantial absence is used it means
20 less than 5% by weight.

Crude terephthalic acid slurry is conventionally synthesized via the liquid phase oxidation of paraxylene in the presence of suitable oxidation catalyst. Suitable catalysts include, but are not limited to, cobalt,

manganese and bromine compounds, which are soluble in the selected solvent. In one embodiment of the invention the catalyst comprises cobalt, bromine and manganese. The cobalt and manganese combined can be in concentrations of about 150 ppm to about 3200 ppm by weight in the crude
5 carboxylic acid slurry. The bromine can be in concentrations of about 10 ppm to about 5000 ppm by weight in the crude carboxylic acid slurry. Preferably, the cobalt and manganese combined can be in concentrations of about 1050 ppm to about 2700 ppm by weight in the crude carboxylic acid slurry. The bromine can be in concentrations of about 1000 ppm to
10 about 2500 ppm by weight in the crude carboxylic acid slurry.

The crude carboxylic acid slurry in conduit **30** is fed to a solid-liquid displacement zone **40** capable of removing a portion of the liquid contained in the crude carboxylic acid slurry **30** to produce the slurry product in conduit **70**. A portion means at least 5% by weight of the liquid is removed.
15 The removal of a portion of the liquid to produce a slurry product in conduit **70** can be accomplished by any means known in the art. Typically, the solid-liquid displacement zone **40** comprises a solid-liquid separator that is selected from the group consisting of a decanter centrifuge, rotary disk centrifuge, belt filter, rotary vacuum filter, and the like. The crude carboxylic
20 acid slurry in conduit **30** is fed to the solid-liquid displacement zone **40** comprising a solid-liquid separator. The solid-liquid separator is operated at temperatures between about 50°C to about 200°C, preferably 140°C to about 170°C. The solid-liquid separator is operated at pressures between

about 30 psig to about 200 psig. The solid-liquid separator in the solid-liquid displacement zone **40** may be operated in continuous or batch mode, although it will be appreciated that for commercial processes, the continuous mode is preferred.

5 The impurities are displaced from the solid-liquid displacement zone **40** in a mother liquor and withdrawn via line **60**. In one embodiment of the invention, additional solvent is fed to the solid-liquid displacement zone **40** via line **50** to reslurry the crude carboxylic acid slurry **30** and form a slurry product **70**. The mother liquor **60** is withdrawn from solid-liquid
10 displacement zone **40** via line **60** and comprises a solvent, typically acetic acid, catalyst, and bromine compounds. The mother liquor in line **60** may either be sent to a process for separating impurities from oxidation solvent via lines not shown or recycled to the catalyst system via lines not shown. One technique for impurity removal from the mother liquor **60** commonly
15 used in the chemical processing industry is to draw out or "purge" some portion of the recycle stream. Typically, the purge stream is simply disposed of or, if economically justified, subjected to various treatments to remove undesired impurities while recovering valuable components. Examples of impurity removal processes include U.S. Patent # 4,939,297 and U.S.
20 Patent 4,356,319, herein incorporated by reference.

Step (b) comprises oxidizing the slurry product **70** in a staged oxidation zone **80** to form a staged oxidation product **110**.

In one embodiment of the invention, the slurry product **70** is withdrawn via line **70** to a staged oxidation zone **80** where it is heated to between about 190°C to about 280°C and preferably between about 200°C to about 250°C and further oxidized with air fed by line **100** to produce a staged oxidation product **110**.

The staged oxidation zone **80** comprises at least one staged oxidation reactor vessel. The slurry product **70** is fed to the staged oxidation zone **80**. The term "staged" means that the oxidation occurs in both the primary oxidation zone **20** discussed previously as well as in the staged oxidation zone **80**. For example, the staged oxidation zone **80** can comprise staged oxidation reactor vessels in series.

When the carboxylic acid is terephthalic acid, the staged oxidation zone **80** comprises an oxidation reactor that is heated to between about 190°C to about 280°C, preferably between about 200°C to about 250°C, and most preferably between 205 °C to 225°C and further oxidized with air or a source of molecular oxygen fed by line **100** to produce a staged oxidation product **110**. Generally, oxidation in the staged oxidation zone **80** is at a higher temperature than the oxidation in the primary oxidation zone **20** to enhance the impurity removal. The staged oxidation zone **80** can be heated directly with solvent vapor, or steam via conduit **90** or indirectly by any means known in the art. Purification in the staged oxidation zone takes place by a mechanism involving recrystallization or crystal growth and oxidation of impurities.

Additional air or molecular oxygen may be fed via conduit **100** to the staged oxidation zone **80** in an amount necessary to oxidize a substantial portion of the partially oxidized products such as 4-carboxybenzaldehyde (4-CBA) in the crude carboxylic acid slurry **30** or slurry product **70** to the corresponding carboxylic acid. Generally, at least 70% by weight of the 4-CBA is converted to terephthalic acid in the staged oxidation zone **80**. Preferably, at least 80% by weight of the 4-CBA is converted to terephthalic acid in the staged oxidation zone **80**. Significant concentrations of 4-carboxybenzaldehyde and p-toluic acid in the terephthalic acid product are particularly detrimental to polymerization processes as they may act as chain terminators during the condensation reaction between terephthalic acid and ethylene glycol in the production of polyethylene terephthalate(PET). Typical terephthalic acid product contains on a weight basis less than about 250 parts per million (ppm) 4-carboxybenzaldehyde and less than about 150 ppm p-toluic acid

Impurities in the crude carboxylic acid slurry **30** or slurry product **70** go into solution as the terephthalic acid particles are dissolved and re-crystallized in staged oxidation zone **80**. Offgas from the staged oxidation zone **80** is withdrawn via line **105** and fed to a recovery system where the solvent is removed from the offgas comprising volatile organic compounds (VOCs). VOCs including methyl bromide may be treated, for example by incineration in a catalytic oxidation unit. The staged oxidation product **110** from the staged oxidation zone **80** is withdrawn via line **110**.

Step (c) comprises crystallizing the staged oxidation product **110** in a crystallization zone **120** to form a crystallized product **160**. Generally, the crystallization zone **120** comprises at least one crystallizer. Vapor product from the crystallization zone can be condensed in at least one condenser and returned to the crystallization zone. Optionally, the liquid from the condenser or vapor product from the crystallization zone can be recycled, or it can be withdrawn or sent to an energy recovery device. In addition, the crystallizer offgas is removed via line **170** and can be routed to a recovery system where the solvent is removed and crystallizer offgas comprising VOCs may be treated, for example by incineration in a catalytic oxidation unit.

When the carboxylic acid is terephthalic acid, the staged oxidation product **110** from the staged oxidation zone **80** is withdrawn via line **110** and fed to a crystallization zone **120** comprising at least one crystallizer where it is cooled to a temperature between about 110°C to about 190°C to form a crystallized product **160**, preferably to a temperature between about 140°C to about 180°C, most preferably about 150°C to about 170°C.

The crystallized product **160** from the crystallization zone **120** is withdrawn via line **160**. Typically, the crystallized product **160** is then fed directly to a vessel and cooled to form a cooled purified carboxylic acid slurry **210**. When the carboxylic acid is terephthalic acid, the cooled crystallized purified carboxylic acid slurry **210** is cooled in a vessel to typically a temperature of approximately 90° C or less before being

introduced into a process for recovering the terephthalic acid as a dry powder or wet cake.

Step (d) comprises cooling the crystallized product in a cooling zone **200** to form a cooled purified carboxylic acid slurry **210**.

5 The crystallized product **160** is withdrawn from the crystallization zone **120** via line **160**. The crystallized product **160** is fed to a cooling zone **200** and cooled to less than about 90 °C to form the cooled purified carboxylic acid slurry **210**. The cooling of the purified carboxylic acid slurry can be accomplished by any means known in the art, typically the cooling
10 zone **200** comprises a flash tank.

Step (e) comprises filtering and optionally drying the cooled purified carboxylic acid slurry **210** in a filtration and drying zone **220** to remove a portion of the solvent from the cooled purified carboxylic acid slurry **210** to produce the purified carboxylic acid product **230**.

15 The cooled, purified carboxylic acid slurry **210** is withdrawn from cooling zone **200** and fed to a filtration and drying zone **220**. A portion of the solvent and remaining catalyst and impurities is separated, and the purified carboxylic acid product is withdrawn via line **230**.

20 The filtration and drying zone **220** comprises a filter suitable for recovering the solid carboxylic acid and a dryer. The filtration can be accomplished by any means known in the art. For example, a rotary vacuum filter can be used for the filtration to produce a filtration cake. The filtration cake goes through an initial solvent removal step, is then rinsed

with acid wash to remove residual catalyst, and then solvent removed again before being sent to the dryers. The drying of the filter cake can be accomplished by any means known in the art that's capable of evaporating at least 10% of the volatiles remaining in the filter cake to produce the
5 carboxylic acid product. For example, a Single Shaft Porcupine® Processor dryer can be used.

The purified carboxylic acid product **230** has a b^* less than about 4.5. Preferably, the b^* color of the purified carboxylic acid product **230** is less than about 3.5. Most preferably, the b^* color in purified carboxylic acid
10 product **230** is less than about 3. The b^* color is one of the three-color attributes measured on a spectroscopic reflectance-based instrument. The color can be measured by any device known in the art. A Hunter Ultrascan XE instrument in reflectance mode is typically the measuring device. Positive readings signify the degree of yellow (or absorbance of blue), while
15 negative readings signify the degree of blue (or absorbance of yellow).

It should be appreciated that the process zones previously described can be utilized in any other logical order to produce the purified carboxylic acid product. It should also be appreciated that when the process zones are reordered that the process conditions may change.

20 In another embodiment of this invention each embodiment can optionally include an additional step comprising decolorizing the carboxylic acid or an esterified carboxylic acid via hydrogenation.

The decolorizing of the purified carboxylic acid slurry or an esterified carboxylic acid can be accomplished by any means known in the art and is not limited to hydrogenation. However, for example in one embodiment of the invention, the decolorizing can be accomplished by reacting a

5 carboxylic acid that has undergone esterification treatment , for example with ethylene glycol, with molecular hydrogen in the presence of a hydrogenation catalyst in a reactor zone to produce a decolorized carboxylic acid solution or a decolorized ester product. For the reactor zone, there are no special limitations in the form or construction thereof,

10 subject to an arrangement that allows supply of hydrogen to effect intimate contact of the carboxylic acid or ester product with the catalyst in the reactor zone. Typically, the hydrogenation catalyst is usually a single Group VIII metal or combination of Group VIII metals. Preferably, the catalyst is selected from a group consisting of palladium, ruthenium,

15 rhodium and combination thereof. The reactor zone comprises a hydrogenation reactor that operates at a temperature and pressure sufficient to hydrogenate a portion of the characteristically yellow compounds to colorless derivatives

EXAMPLES

This invention can be further illustrated by the following example of preferred embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated.

Example

Paraxylene was oxidized at 160°C utilizing a Co, Mn, Br catalyst system to produce a crude terephthalic acid slurry having 30-35% solids. The crude terephthalic acid slurry was crystallized and purified using the process shown in Figure 1. with the omission of a hydrogenation step and the crystallized product from the crystallization zone 120 was transferred directly to flash tank. The product was removed after filtration and drying and analyzed for 4-carboxybenzaldehyde(4-CBA), trimellitic acid(TMA), and 2,6-dicarboxyfluorenone(2,6-DCF), percent transmittance and b*. The b* is one of the three-color attributes measured on a spectroscopic reflectance-based instrument. A Hunter Ultrascan XE instrument is typically the measuring device. Positive readings signify the degree of yellow (or absorbance of blue), while negative readings signify the degree of blue (or absorbance of yellow).

The concentrations of 4-CBA, TMA, 2,6-DCF in the terephthalic acid were analyzed via liquid chromatography. To determine the percent

transmittance, a 10% solution of terephthalic acid product in 2M KOH was measured using a UV visible spectrometer at 340nm. The b^* of the terephthalic acid was measured using a reflectance color method at 340nm. The results are shown in Table 1.

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Ex. #	4-CBA ¹ (ppm)	TMA ² (ppm)	2,6-DCF ³ (ppm)	%T ⁴	b^{*5}
1	103	51	10	89	4.1

The amount of 4-CBA present in the purified terephthalic acid product produced by the process of the present invention decreased significantly from typical levels found in the crude carboxylic acid slurry. The typical levels weren't measured during this trial but these levels were known to those skilled in the art to be about what has been previously disclosed wherein the crude carboxylic acid slurry comprising terephthalic acid, typically contains on a weight basis from about 800 to 7,000 parts per million (ppm) 4-carboxybenzaldehyde. The % transmittance of the purified terephthalic acid product has a direct influence on the color of the polyethylene terephthalate (PET) produced. Desirable PTA (purified terephthalic acid) is white (which is referred to as having low color). Higher % transmittance indicates less color in the PTA. The degree of improvement in all the measured categories is particularly surprising given

the simplicity of the centrifugation in the solid-liquid separation zone and that no hydrogenation step was performed. In the past, comparable purity levels have been achieved typically by utilization of a hydrogenation plant which includes numerous steps and pieces of equipment, and significant capital investment.

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The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention